

PATENT SPECIFICATION

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(54) COPPER COATED COMPOSITE POWDERS AND METHOD OF PRODUCTION THEREOF

(71) We, SHERRITT GORDON MINES LIMITED, a Company organized under the laws of Ontario, having its head office at 2800 Commerce Court West, 5 Toronto, Ontario, Canada, do hereby declare the invention for which we pray that a Patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to copper coated composite powders and to a method of production of such powder. The powder with which the invention is particularly concerned is useful as an abradable or hard surface coating material on metallic and non-metallic surfaces.

Wide use is made in industry of powders composed of core particles surrounded by 20 and encased in an outer metallic layer. These powders, referred to herein as "composite powders", are used, for example, in the flame spraying and plasma spraying fields, in the manufacture of strip by roll compaction and 25 in the manufacture of special metal parts by compaction in a die.

The method of production of composite powders depends upon the composition of their coating material and their cores. Coating material can, for example, be applied to metallic core materials by cementation provided the coating material is metallic and is higher in the electro-motive series than the core material. Another method for the production of certain composite powders involves dispersing solid particles of material which is to form the core of the powders in an ammoniacal solution containing a soluble salt of the metal which is to form 35 the coating of the powder. The solution is contacted at elevated temperature and pressure with a reducing gas to cause the coating metal to precipitate and deposit onto the core particles.

Metals which can be deposited on core particles by this method include cobalt, nickel, gold, silver, cadmium and others. The

latter method is described in numerous patents including Canadian patents Nos. 561,828, 562,160 and 632,785.

The production of copper-coated composite particles poses serious technical problems. When copper is precipitated from an ammoniacal solution containing suspended core particles, most of the copper will precipitate in the form of discrete particles separate from the core particles. The little copper which does bond to the core particles will form a discontinuous spotty deposit. Most of the outer surfaces of the core particles will however be completely free of copper.

A much higher quality of copper-coated composite powder can be produced by cementation but metals commercially important as core material and higher than copper in the electromotive series are limited.

The present invention seeks to provide a method by which a uniform coating of copper can be applied to particles of a variety of materials. Specifically, the materials may be metal alloys and elementary metals below copper in the electromotive series. In addition, a wide range of non-metallic materials may be coated with copper by the method of the present invention.

The invention further seeks to provide copper coated metallic and non-metallic particles suitable for use as abradable or hard surface coating material on metallic and non-metallic surfaces.

The method of the present invention broadly involves the steps of providing solid particles of a core material selected from the group comprising: non-metals, metal alloys and elementary metals lower than copper in the electromotive series; forming a slurry of said particles dispersed in an aqueous ammoniacal ammonium salt solution in which said particles are insoluble and which contains dissolved nickel values; reacting said slurry with a reducing gas at elevated temperature and pressure to cause nickel to precipitate from solution and to coat said dis-

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persed particles, terminating the reaction when the weight of nickel coating the dispersed particles is substantially the molecular equivalent of the weight of copper desired
 5 in the coating of the finished composite powder; and dispersing said nickel coated particles in a solution having a pH no higher than 7 and containing dissolved copper values to cause cementation of copper onto the core particles with concurrent dissolution of substantially the entire nickel coating.

The product of the invention may be characterized as a powder composition consisting of metallic or non-metallic core particles coated with copper. Especially useful and novel powder compositions within the class are composite particles consisting of particles of calcium fluoride, molybdenum disulphide, cobalt oxide or diatomaceous earth coated with copper.

The invention will now be described further by way of example with reference to the accompanying drawing which shows graphically changes in concentration of nickel and copper in solution during the cementation reaction.

Since the subject invention seeks to provide a method of applying a coating of copper to material which cannot be coated with copper by cementation, the material of which the starting particles of the invention is composed will normally be restricted to such material. The material of the starting particles will also be restricted to ones which are insoluble in a nickel-containing ammoniacal ammonium salt solution subjected to gas reduction at elevated temperature pressure.

There exists a very large number of materials having the properties described in the preceding paragraph. The core material may be composed of elementary metals lower than copper in the electromotive series. Examples of such metals are silver, platinum, gold and lead. The core material may also be composed of metal alloys or it may be composed of non-metals such as refractory oxides, nitrides, borides, graphite, diamonds and all other crystalline forms of carbon. Also, the core material may be composed of calcium fluoride, diatomaceous earth, molybdenum disulphide, cobalt oxide, silica, boron nitride and carbides such as chromium carbide and tungsten carbide.

The starting particles must be sufficiently small that they will remain in suspension in an agitated solution. In general, the particles of about 32 mesh standard Tyler screen or smaller meet this requirement where the specific gravity of the particles is less than about 10. Where the particles have a higher specific gravity their size should generally not exceed about 100 mesh. However the shape of the particles will have a bearing on whether they can be kept in suspension, thus

there is no hard and fast relationship between particle size and specific gravity.

The first step in the process of the subject invention is to apply a coating of nickel onto the core material. The method doing so is known and is described in the Canadian patents mentioned before. Since the method is known, it will be only briefly summarized herein. According to the method, the core particles are dispersed in an ammoniacal ammonium salt solution containing dissolved nickel values. The resulting slurry is reacted at elevated temperature, usually 250°F. or over with a reducing gas, usually hydrogen, under a partial pressure of 100 p.s.i. or over. The reaction results in precipitation of nickel from solution and deposition thereof as a continuous coating onto the particles of the core material.

The quantity of nickel which is deposited onto the core particles should be substantially the molecular equivalent of the quantity of copper desired on the finished composite particles. For example, assume that it is required to produce 100 grams of finished composite particles of which the copper coating is to account for approximately 80% of the total weight and the core is to account for the balance. The finished particles must therefore contain 80 grams or 1.26 moles of copper. The nickel-coated particles from which the finished composite particles are produced must also contain approximately 1.26 moles of nickel or 74 grams of nickel. Thus, approximately 74 grams of nickel should be deposited onto the core particles.

It is generally found desirable to adjust the concentration of the nickel in ammoniacal solution according to the quantity of nickel which is desired to be deposited on the core particles. Under normal conditions, dissolved nickel values in the solution can be decreased to below 1 gram per litre very easily. Thus, it is only necessary to adjust the concentration of nickel in the ammoniacal solution such that there is a slight excess of nickel values over the amount of nickel desired to be precipitated, generally about 1 gram per litre. For example, to prepare the composite particles described in the preceding paragraph, a given amount of core material e.g. 20 grams is suspended in a nickel-containing solution. The solution should contain 74 grams of dissolved nickel plus an additional 1 gram of nickel per litre of solution.

The concentration of nickel in the ammoniacal solution must be below that at which crystallization of the nickel values occurs. Where the nickel values are in the form of nickel sulphate, the concentration of the nickel sulphate should be between 25 and 75 grams per litre. Preferably, the concentration should be maintained at about 50 grams per litre. The reaction is terminated

when the desired amount of nickel has deposited onto the core particles. Where the solution is initially only provided with a slight excess of dissolved nickel over the amount desired to be precipitated, the reaction is of course terminated when the solution is substantially depleted of nickel values. When the solution is depleted, the consumption of hydrogen ceases. Usually, hydrogen is no longer consumed after 15 to 30 minutes from commencement of reduction at the preferred operating conditions.

Following deposition of nickel on the core material, the resulting composite particles are separated from solution, by for example, filtration and are then dispersed in an aqueous solution having a pH of no higher than 7 and containing dissolved copper values. The copper values in solution may be in the form of copper sulphate or copper chloride and will desirably be in slight excess over the amount which is to be cemented onto the particles. For example, if 80 grams of copper are to be cemented onto the particles, the solution may contain 80 grams of copper plus an additional 1 to 5 grams of copper per litre of solution.

The cementation reaction will generally, in practice, be carried out at temperatures in the range of about 100° to 300°F. The principal reaction which occurs during cementation (where cementation takes place in an aqueous sulphuric acid solution) is as follows:



The cementation reaction is preferably conducted under a hydrogen overpressure of from about 50 to about 500 p.s.i.g. to displace the equilibrium of a reversible side reaction so that formation of a product which tends to diminish the quality of the finished composite particles is suppressed. The side reaction which occurs concurrently with reaction (1) is as follows:



Hydrogen is believed to shift the equilibrium of reaction (2) to favour the production of metallic copper. As a result, copper which displaces nickel according to reaction (1) and which cements onto the core particles tends to remain intact. The finished composite particles will have a uniform continuous coating of copper and are highly desirable for this reason.

In the absence of hydrogen, reaction (2) tends to proceed to the right so that the deposit of copper on the core particles reacts with sulphuric acid. As a result, the copper deposited on the core particles at the completion of the cementation reaction represents only a portion of the total cop-

per content of the solution at the beginning of the reaction. Since it is difficult to control the proportion of copper initially in solution which deposits onto the core particles, the cementation reaction should be conducted in the presence of hydrogen so that the finished composite powder will have the desired copper content.

The cementation reaction is usually complete in about 30 to 60 minutes depending on temperature. Where the concentration of copper in the solution is adjusted according to the quantity of copper which is to be cemented onto the particles, the reaction will, of course, be complete when the solution is substantially depleted of copper. Upon completion of the cementation reaction, the finished copper coated particles are separated from solution by means of, for example, filtration.

The finished composite particles can be used in a number of ways depending upon the composition of the core material. They can, for example, be used as abradable coating material such as abradable seals. In such event, the core material must be abradable, erosion resistant and corrosion resistant in the environment in which the particles are used. Suitable core materials for this purpose include graphite diatomaceous earth, calcium fluoride, molybdenum disulphide, cobalt oxide and boron nitride. Because graphite oxidizes at low temperatures, its use as a core material in engine seals composed of copper coated particles is limited to temperatures up to about 1022°F. For higher service temperatures, composite powders having more refractory abradable cores are required. Diatomaceous earth and calcium fluoride are suitable for this purpose.

The finished composite particles can also be used as coating material to impart a hard wear resistant characteristic to a substrate. Particles suitable for this purpose will have a core composed of a refractory oxide such as alumina or a carbide of such element as chromium, tungsten, or titanium.

The following example illustrates the effect of hydrogen pressure on the properties of the finished copper coated composite particles.

EXAMPLE

The starting material for this example was nickel-coated graphite composite powder prepared according to the procedure described in Canadian Patent No. 632,785. The composite powder was made up of 80% nickel and 20% graphite by weight and had the following screen analysis (standard Tyler scale): +100 mesh: trace; -100 +200 mesh; 10% -200 +325 mesh; 50.0%; -325 mesh: 40.0%.

Samples of the powder were dispersed in an autoclave containing from 100—210 g.p.l. copper sulphate in solution. The resulting

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slurries were heated to 300°F., in some cases under an overpressure of hydrogen of 350 p.s.i.g. and in other cases in the absence of a hydrogen overpressure. The solution was analyzed for nickel and copper at various times during heating and the results are illustrated in the drawing.

The results show that hydrogen pressure promotes the cementation reaction. After 60 minutes, the concentration of nickel in solution at 0 p.s.i.g. H₂ overpressure is 0.31 moles per litre while at 350 p.s.i.g. H₂ the concentration is 0.52 moles per litre. The contraction of copper in solution at 0 and 350 p.s.i.g. H₂ overpressure after 60 minutes is 0.2 and 0.05 moles per litre respectively. Thus, a higher proportion of nickel displaces copper from solution under a hydrogen overpressure than in the absence of hydrogen.

WHAT WE CLAIM IS:—

1. A method of producing a copper-coated composite powder which comprises: providing solid particles of a core material selected from the group comprising: non-metals, metal alloys and elementary metals lower than copper in the electromotive series; forming a slurry of said particles dispersed in an aqueous ammoniacal ammonium salt solution in which said particles are insoluble and which contains dissolved nickel values; reacting said slurry with a reducing gas at elevated temperature and pressure to cause nickel to precipitate from solution and to coat said dispersed particles; terminating the reaction when the weight of nickel coating the dispersed particles is substantially the molecular equivalent of the weight of copper desired in the coating of the finished composite powder; and dispersing said nickel-coated particles in a solution having a pH no higher than 7 and containing dissolved copper values to cause cementation of copper onto the core particles with concurrent dissolution of substantially the entire nickel coating.

2. A method of producing a copper-coated composite powder which comprises: providing solid particles of a core material selected

from the group comprising: non-metals, metal alloys and elementary metals lower than copper in the electromotive series; forming a slurry of said particles dispersed in an aqueous ammoniacal ammonium salt solution in which said particles are insoluble and which contains dissolved nickel values of a weight slightly in excess of the molecular equivalent of the weight of copper desired in the coating of the finished composite powder; reacting said slurry with a reducing gas at elevated temperature and pressure to cause nickel to precipitate from solution and to coat said dispersed particles; terminating the reaction when the solution is substantially depleted of dissolved nickel values; and dispersing said nickel-coated particles in a solution having a pH no higher than about 7 and containing dissolved copper values to cause cementation of copper onto the core particles with concurrent dissolution of substantially the entire nickel coating.

3. The method as claimed in claims 1 or 2 further including contacting said copper-containing solution in which said nickel-coated particles are dispersed with hydrogen gas under a pressure of from about 50 to about 500 p.s.i.g.

4. The method as claimed in claims 1 or 2 further including contacting said copper-containing solution in which said nickel pressure of from about 50 to about 350 p.s.i.g.

5. A powder composition having a layer of copper within which a central core is encased, said core being composed of a material selected from the group comprising: calcium fluoride, molybdenum disulphide, cobalt oxide and diatomaceous earth.

6. A method of producing a copper-coated composite powder as claimed in Claim 1 and substantially as hereinbefore described.

7. A powder composition as claimed in Claim 5 and substantially as hereinbefore described.

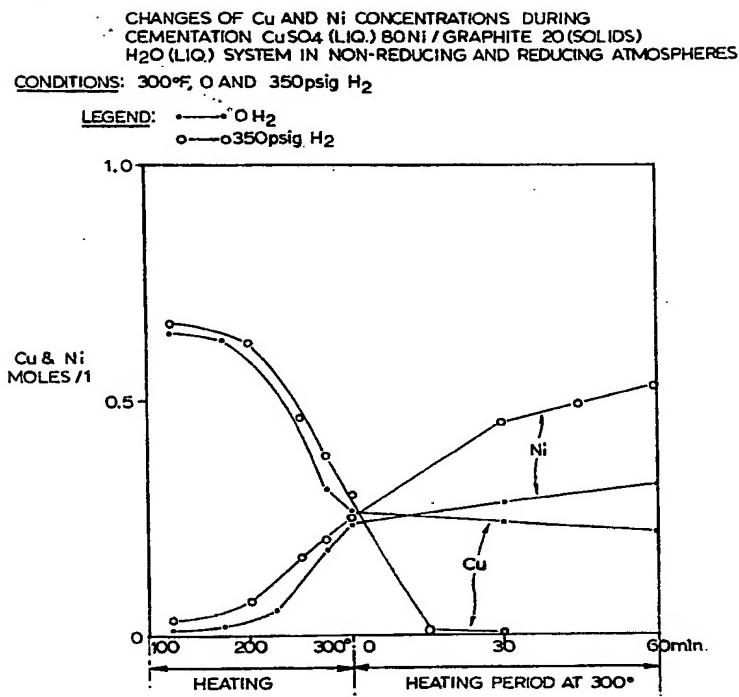
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COMPLETE SPECIFICATION

1 SHEET

*This drawing is a reproduction of
the Original on a reduced scale*

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